

Sumanenyl Metallocenes: Synthesis and Structure of Mono- and Trinuclear Zirconocene Complexes

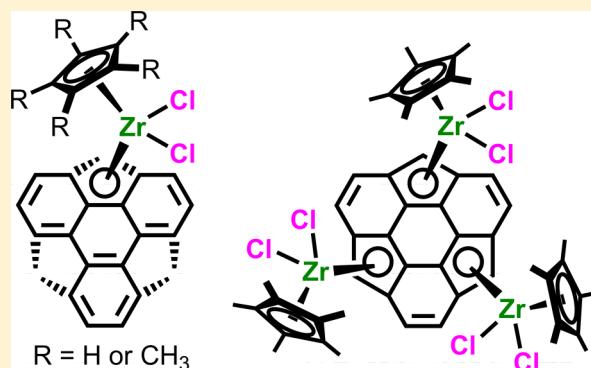
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S Supporting Information

ABSTRACT: Mono- and trinuclear sumanenyl zirconocene complexes Cp(sumanenyl)ZrCl₂, Cp*(sumanenyl)ZrCl₂, and (C₂₁H₉)[(Cp*)ZrCl₂]₃ were successfully synthesized. In the mononuclear complexes, convex binding with disturbed η⁵-bonding was confirmed in a solid state. As demonstrated in the trinuclear complex, the multibenzyl anion of sumanene offers a novel ligand for the multinuclear metallocenes.



1. INTRODUCTION

Coordination of curved carbon π surfaces to metals has been of fundamental interest in view of coordination modes and molecular shapes since the report of a metal complex of C₆₀.^{1–4} Open-end molecular bowls shown by fullerenes' fragments (geodesic polyarenes, buckybowls, or π bowls; here we use π bowls) also possess curved carbon π surfaces, which are represented by corannulene and sumanene (**1**, Figure 1a).^{5,6} From a coordination chemistry viewpoint, π bowls are quite unique because they can provide not only convex surfaces but open concave surfaces for metal binding. In this context, these studies attract the broad interest with future potential as catalysts and materials. π -Bowl complexes of various transition metals in several coordination modes have been prepared and characterized for over 17 years mainly using corannulene and corannulene derivatives as a ligand.⁷ Mono- and multialkali metals complexes of corannulene also have been studied for over two decades.⁸ We have studied π -bowl complexes with sumanene ligand.⁹ The concave-binding complex [CpFe(η^6 -sumanene)]PF₆ (Cp = C₅H₅) was demonstrated in both solution and solid states,^{9a} which is the first report of the selective concave binding for a π bowl ligand. Its chiral complex was also demonstrated.^{9b} Furthermore, the dynamic bowl-to-bowl inversion behavior was revealed in [CpRu(η^6 -sumanene)]PF₆.^{9d}

In π -bowl complexes, however, the metallocene-type complexes have been less studied so far despite their potential for catalyst application in addition to the unique structural properties. The only examples include zirconocene and titanocene complexes with the fluorenyl-type ligand prepared via hydrogenation of corannulene.¹⁰ In the organometallic chemistry of fullerene, there have been reported metallocene

complexes with the cyclopentadienyl-type ligand prepared via collapsing of fullerene π conjugation since the development of buckyferrocene by Nakamura and co-workers.¹¹ The dinuclear metallocene complexes were also reported by them.¹² We have revealed that sumanenyl mono-, di- and trianions can be generated selectively by treatment with a strong base.¹³ Such cyclopentadienyl-like anion is considered to provide mono- and even multinuclear metallocene-type complexes (Figure 1b). In the present study, mono- and trinuclear zirconocene complexes **2a**, **2b**, and **3** are set as synthetic targets to demonstrate the sumanenyl metallocenes (Figure 1c). Here, we report the synthesis of sumanenyl zirconocene complexes **2a**, **2b**, and **3**.

2. RESULTS AND DISCUSSION

Complexation reactions were followed by ¹H NMR. To generate benzylic monoanion of **1**, *n*-BuLi was employed instead of *t*-BuLi. Treatment of **1** with *n*-BuLi (1.0 equiv) in THF-*d*₈ gave the corresponding benzylic monoanion. Then, the reaction of monoanion with CpZrCl₃ (1.0 equiv) was performed at room temperature for 10 min to afford the red-brown solution of the zirconocene complex **2a** (Scheme 1a). Yield of **2a** was 90%, calculated by the integral ratio [**2a**/(**2a** + **1**) × 100] of the crude mixture. Crystallization from toluene/hexane afforded **2a** as an orange solid in 15% isolated yield. In the similar manner, the deep green solution of Cp*(sumanenyl)ZrCl₂ (**2b**, Cp* = C₅Me₅) with Cp* ligand instead of Cp one was obtained in 90% yield (Scheme 1a).

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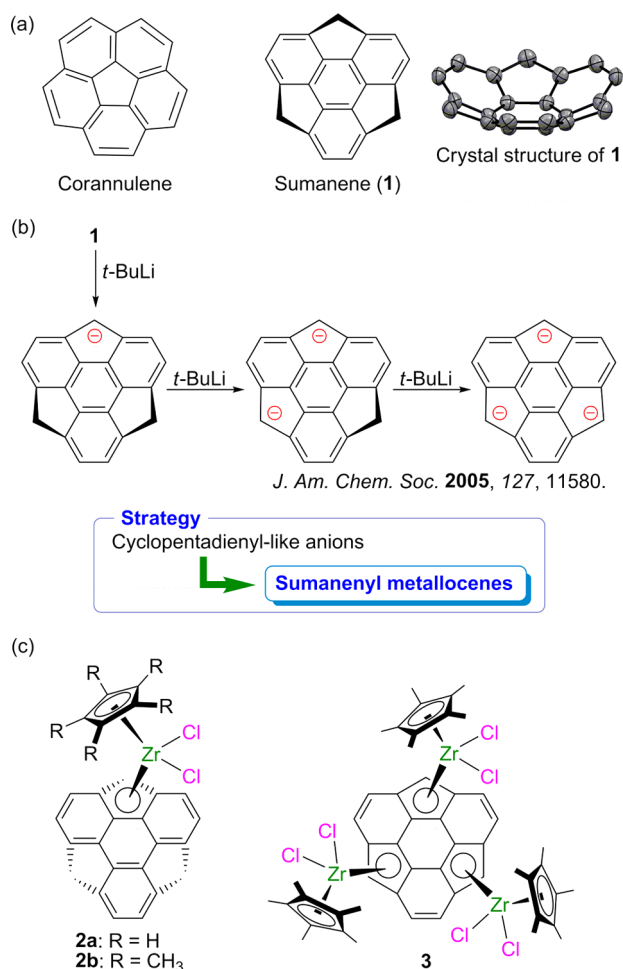
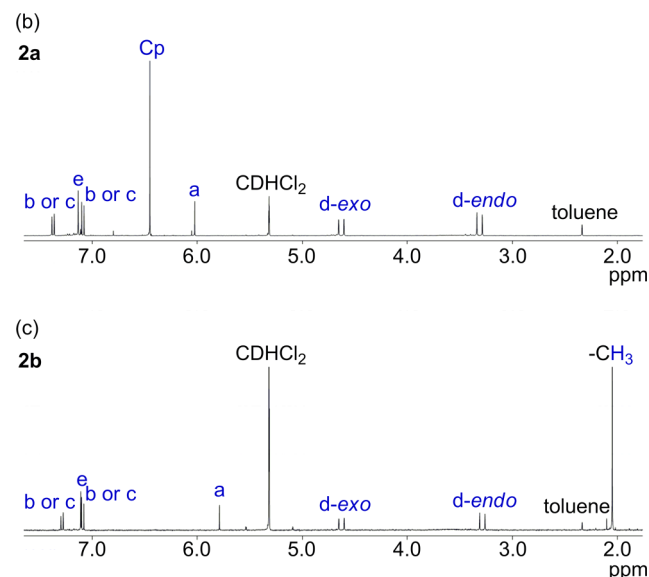
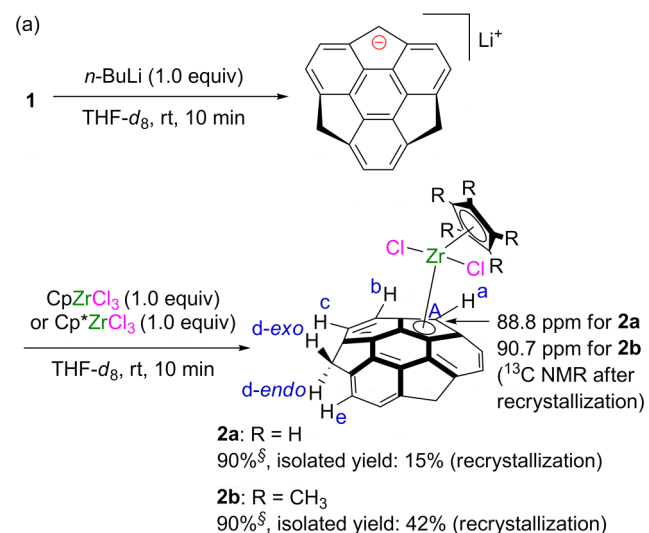


Figure 1. (a) Corannulene and sumanene (1), and crystal structure of 1. (b) Selective generation of mono-, di-, and tribenzylic anions of 1, and a synthetic strategy of sumanenyl metallocenes. (c) Mononuclear sumanenyl zirconocene complexes 2a and 2b, and trinuclear zirconocene complex 3.

Crystallization from toluene/CH₂Cl₂ afforded 2b as a red solid in 42% isolated yield.

The ¹H NMR spectra for 2a and 2b after recrystallization are given in Scheme 1b,c, respectively. Both spectra showed a pair of doublets for the benzylic protons [$\delta = 4.63$ ($J = 20.2$ Hz, *d-exo*) and 3.31 ($J = 20.2$ Hz, *d-endo*) ppm for 2a, and $\delta = 4.63$ ($J = 20.2$ Hz, *d-exo*) and 3.29 ($J = 20.2$ Hz, *d-endo*) ppm for 2b, respectively], a singlet for Ha [($\delta = 6.03$ ppm for 2a and $\delta = 5.79$ ppm for 2b, respectively)], and a pair of doublets and a singlet in the aromatic region. Thus-observed large separation of the chemical shifts for the *exo*- and *endo*-benzylic protons is typical in the bowl-shaped sumanene derivatives,^{6b} which can be accounted for by the ring current effect. The peaks for both Cp and methyl protons of Cp* were observed as a singlet, indicating the fast rotation of the Cp rings compared to the NMR time scale at room temperature. As a whole, both spectra for 2a and 2b show C_s symmetric structures. The η^1 , η^3 , and η^5 -hapticity can be taken in the coordination of the fluorenyl ligands to Zr atom. According to the literatures,¹⁴ an indication to classify them in solution using ¹³C chemical shift of C₉ position in a fluorenyl ligand was reported: for the η^1 case $\delta = 68$ ppm, for the η^3 case $\delta = 78$ ppm, and for the η^5 case $\delta =$ around 100 ppm. The diagnostic carbon A in 2a and 2b are $\delta = 88.8$ and 90.7 ppm, respectively (Scheme 1a), ranging between

Scheme 1. (a) Synthesis of 2a and 2b; (b) ¹H NMR Spectrum of 2a after Recrystallization; (c) ¹H NMR Spectrum of 2b after Recrystallization



^SYields based on the integral ratio in the in situ ¹H NMR spectra after the reactions {2a (or 2b)/[2a (or 2b) + 1] × 100} of the crude mixture.

η^3 - and η^5 -hapticity. However, both complexes 2a and 2b are likely to have more η^5 -bonding character than the corresponding fluorenyl complexes Cp(fluorenyl)ZrCl₂¹⁵ and Cp*(fluorenyl)ZrCl₂¹⁶ ($\delta = 85.0$ and 83.3 ppm, respectively). To investigate the face selectivity of the coordination, the chemical shifts for Cp and methyl protons of Cp* were compared to those for the corresponding fluorenyl complexes Cp(fluorenyl)ZrCl₂¹⁵ and Cp*(fluorenyl)ZrCl₂¹⁶. The signal of the Cp protons of 2a at $\delta = 6.46$ ppm was shifted $\Delta\delta = 0.35$ ppm to the lower field than the corresponding protons of Cp(fluorenyl)ZrCl₂ ($\delta = 6.11$ ppm). This lower-field shift can be explained by the antishielding effect of the ring current, suggesting the convex binding. In the case of 2b, the slightly lower field shift of the methyl protons of Cp* group ($\Delta\delta = 0.05$ ppm) from the corresponding protons of Cp*(fluorenyl)ZrCl₂

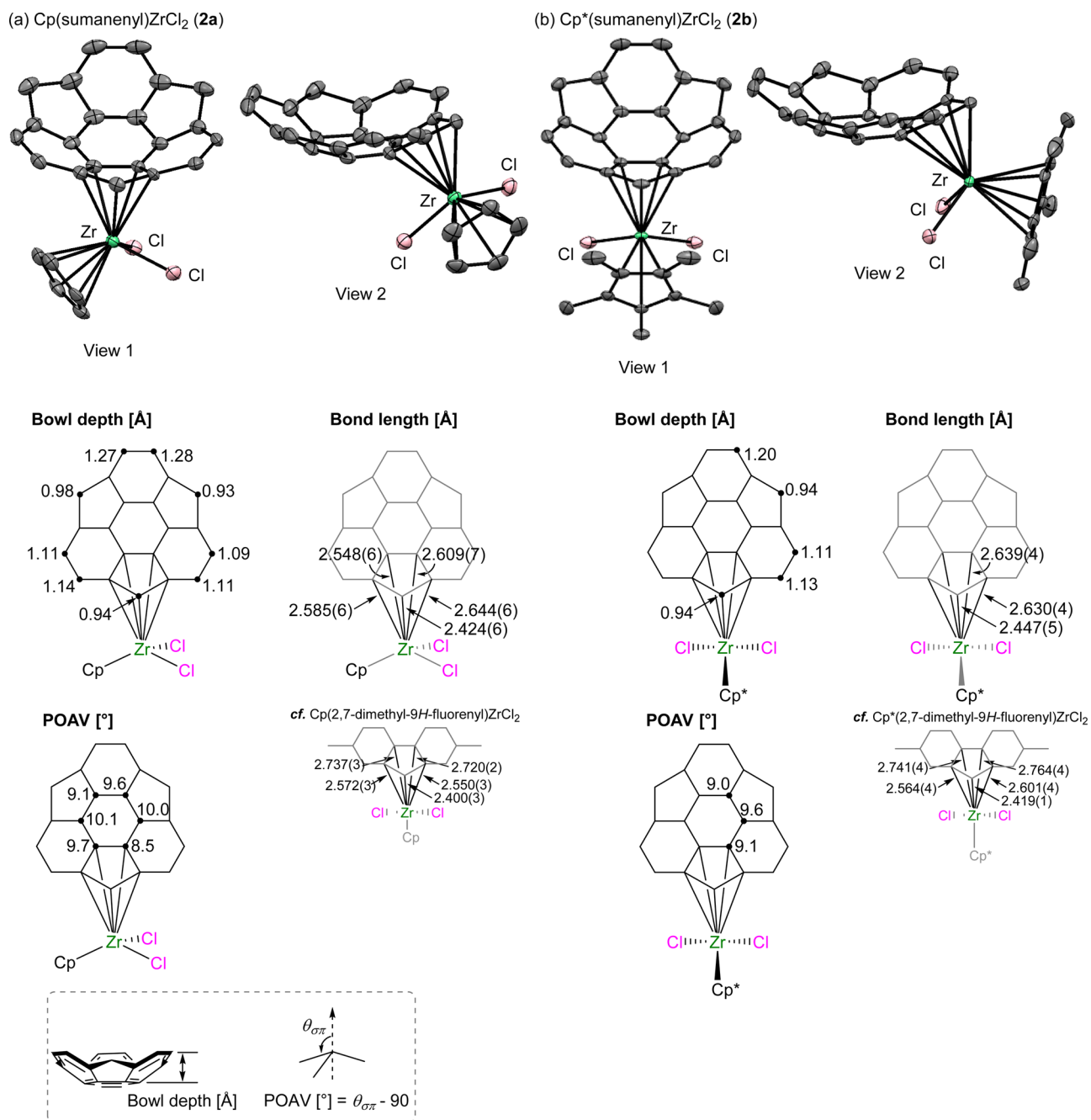


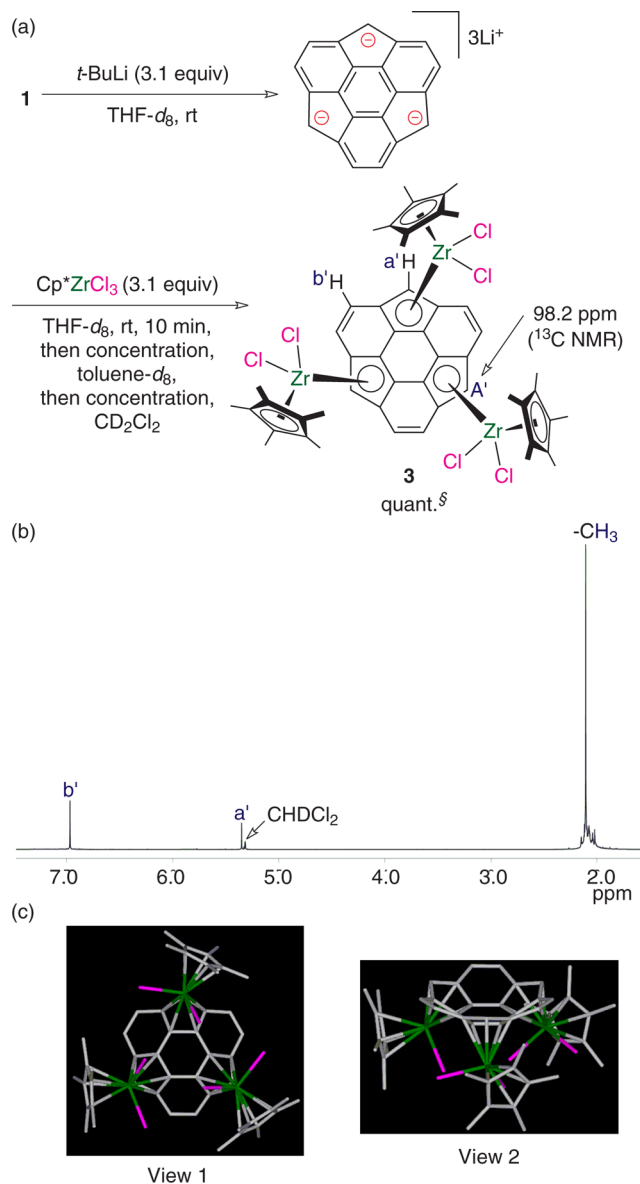
Figure 2. ORTEP drawings (thermal ellipsoids set at the 50% probability level), bowl depth, POAV, and bond length of the sumanenyl ligands to Zr for (a) **2a** and (b) **2b**.

($\delta = 2.00$ ppm) was observed, which may also suggest the convex binding.

Recrystallization of **2a** and **2b** from CH₂Cl₂/hexane afforded the orange and red single crystals suitable for X-ray diffraction, respectively. The ORTEP diagrams for **2a**¹⁷ and **2b**¹⁸ determined by X-ray crystallographic analysis are illustrated in Figure 2a,b, respectively, and clearly show the convex binding of CpZr and Cp*Zr units to the sumanenyl ligand. There is difference between **2a** and **2b** in the symmetry (**2a**: no symmetry, **2b**: C_s symmetry). The bowl depth was measured as a perpendicular distance from the bottom plane of sumanene skeleton to the benzylic carbon atoms of the five-membered rings or the rim carbon atoms of the six-membered rings (Figure 2a). In both complexes, a small extent of bowl

deepening was observed around the coordinated site (five-membered ring: around 0.94 Å, six-membered rings: 1.09–1.28 Å) compared to **1** (five-membered ring: 0.90 Å, six-membered rings: 1.11 Å). π -Orbital axis vector (POAV) angle¹⁹ was employed to evaluate the curvature. POAV angle is defined as $\theta_{\sigma\pi} - 90$ (Figure 2a), which indicates the extent of the pyramidalization. Selected values are depicted in Figure 2a,b. POAVs for **2a** and **2b** at the hub benzene ring range from 8.5 to 10.1°, which are the slightly larger values compared to that for **1** (8.8°). The bond lengths of the sumanenyl ligand to Zr for **2a** and **2b** are shown in Figure 2a, which range from 2.42 to 2.64 Å. The trends are similar to those for the analogous disturbed η^5 -bonding complexes Cp(2,7-dimethyl-9H-fluorenyl)ZrCl₂ (2.40 to 2.74 Å)¹⁵ and Cp*(2,7-dimethyl-9H-fluorenyl)ZrCl₂

Scheme 2. (a) Synthesis, (b) ^1H NMR Spectrum, and (c) Optimized Structure of 3 (C, H, Cl: B3LYP/3-21G; Zr: B3LYP/LANL2DZ)



[§]Judging from the ^1H NMR spectrum of the crude product shown in (b).

(2.42 to 2.76 Å)¹⁶ as shown in Figure 2a,b, however, the sumanenyl complexes have more η^5 -bonding character. In the packing structure of **2a**, the enantiomers based on the distortion of Cp ring are alternately arranged (see Figure S1a in the Supporting Information). On the other hand, CH/ π interaction between methyl protons of Cp* and cyclopentadienyl-like moiety of sumanenyl ligand was observed, inducing the columnar packing of **2b** (see Figure S1b in the Supporting Information).

Trinuclear sumanenyl zirconocene was also synthesized to demonstrate the multinuclear sumanenyl metallocenes. The reactions were followed by ^1H NMR. Treatment of **1** with *t*-BuLi (3.1 equiv) in THF-*d*₈ gave the corresponding benzylic trianion. Then, the trianion reacted with Cp*ZrCl₃ (3.1 equiv) at room temperature for 10 min to afford the blackish green solution of the trinuclear zirconocene complex **3** (Scheme 2a).

After the reaction, THF-*d*₈ was immediately replaced by toluene-*d*₈ because the obtained complex is less stable in THF-*d*₈. Then, toluene-*d*₈ was replaced by CD₂Cl₂. This manipulation was effective to remove THF-*d*₈ completely. The ^1H NMR spectrum is shown in Scheme 2b. Only three singlet peaks were observed [δ = 6.97 (6H, Hb'), 5.35 (3H, Ha'), 2.11 (45H, -CH₃) ppm], showing the C₃ symmetry. Judging from the spectrum, the yield is nearly quantitative. In the ^{13}C NMR, the diagnostic carbon A' to estimate the hapticity in **3** was δ = 98.2 ppm (Scheme 2a). This value corresponds to η^5 -hapticity.¹⁴ The face selectivity was not determined at present. However, two possibilities are considered to interpret the observed C₃ symmetric trinuclear η^5 -bonding complex. One is the case of tri-convex binding. The other is the case of tri-concave binding. From the steric bulkiness of the Cp*ZrCl₂ unit, the latter possibility is unlikely. Scheme 2c shows the DFT-optimized structure of the tri-convex η^5 -binding complex (C, H, Cl: B3LYP/3-21G; Zr: B3LYP/LANL2DZ).²⁰

3. CONCLUSION

In conclusion, the mono- and trinuclear sumanenyl zirconocene complexes **2a**, **2b**, and **3** were successfully synthesized. In the mononuclear complexes **2a** and **2b**, convex binding with disturbed η^5 -bonding was confirmed in a solid state. As demonstrated in the trinuclear complex **3**, the multibenzyl anion of sumanene offers to provide a new class of polynuclear metallocene complexes, which will open new perspectives in metallocene chemistry. Zirconocenes have been utilized for a polymerization catalyst,²¹ Negishi carbometalation catalyst,²² and a nitrogen fixation reagent.²³ Study on the catalytic properties of the zirconocene complexes are now underway.

■ ASSOCIATED CONTENT

Supporting Information

Packing structures of **2a** and **2b** (Figure S1). Synthetic procedures and ^{13}C NMR charts of **2a**, **2b**, and **3**. Crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) For a first C₆₀ complex: Fagan, P. J.; Calabrese, J. C.; Malone, B. *Science* **1991**, 252, 1160.
- (2) For a review for fullerene complexes: Balch, A. L.; Olmstead, M. M. *Chem. Rev.* **1998**, 98, 2123.
- (3) For accounts for π -bowl complexes: (a) Petrukhina, M. A.; Scott, L. T. *Dalton. Trans.* **2005**, 2969. (b) Petrukhina, M. A. *Coord. Chem. Rev.* **2007**, 251, 1690.

(4) For a cycloparaphenylene complex: Zabula, A. V.; Filatov, A. S.; Xia, J.; Jasti, R.; Petrukhina, M. A. *Angew. Chem., Int. Ed.* **2013**, *52*, 5033.

(5) (a) Wu, Y.-T.; Siegel, J. S. *Chem. Rev.* **2006**, *106*, 4843.

(b) Tsefrikas, V. M.; Scott, L. T. *Chem. Rev.* **2006**, *106*, 4868.

(c) Petrukhina, M. A.; Scott, L. T. *Fragments of Fullerenes and Carbon Nanotubes*; Wiley: Hoboken, 2012.

(6) (a) Higashibayashi, S.; Sakurai, H. *Chem. Lett.* **2011**, *40*, 122.

(b) Amaya, T.; Hirao, T. *Chem. Commun.* **2011**, *47*, 10524.

(7) (a) Seiders, T. J.; Baldrige, K. K.; O'Connor, J. M.; Siegel, J. S. *J. Am. Chem. Soc.* **1997**, *119*, 4781. (b) Alvarez, C. M.; Angelici, R. J.; Sygula, A.; Sygula, R.; Rabideau, P. W. *Organometallics* **2003**, *22*, 624.

(c) Petrukhina, M. A.; Andreini, K. W.; Mack, J.; Scott, L. T. *Angew. Chem., Int. Ed.* **2003**, *42*, 3375. (d) Vecchi, P. A.; Alvarez, C. M.; Ellern, A.; Angelici, R. J.; Sygula, A.; Sygula, R.; Rabideau, P. W. *Angew. Chem., Int. Ed.* **2004**, *43*, 4497. (e) Petrukhina, M. A.; Andreini, K. W.; Peng, L.; Scott, L. T. *Angew. Chem., Int. Ed.* **2004**, *43*, 5477. (f) Vecchi, P. A.; Alvarez, C. M.; Ellern, A.; Angelici, R. J.; Sygula, A.; Sygula, R.; Rabideau, P. W. *Organometallics* **2005**, *24*, 4543. (g) Petrukhina, M. A.; Sevryugina, Y.; Rogachev, A. Y.; Jackson, E. A.; Scott, L. T. *Angew. Chem., Int. Ed.* **2006**, *45*, 7208. (h) Petrukhina, M. A.; Sevryugina, Y.; Rogachev, A. Y.; Jackson, E. A.; Scott, L. T. *Organometallics* **2006**, *25*, 5492. (i) Siegel, J. S.; Baldrige, K. K.; Linden, A.; Dorta, R. *J. Am. Chem. Soc.* **2006**, *128*, 10644. (j) Filatov, A. S.; Rogachev, A. Y.; Jackson, E. A.; Scott, L. T.; Petrukhina, M. A. *Organometallics* **2010**, *29*, 1231. (k) Bandera, D.; Baldrige, K. K.; Linden, A.; Dorta, R.; Siegel, J. S. *Angew. Chem., Int. Ed.* **2011**, *50*, 865.

(8) (a) Ayalon, A.; Rabinovitz, M.; Cheng, P.-C.; Scott, L. T. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1636. (b) Ayalon, A.; Sygula, A.; Cheng, P.-C.; Rabinovitz, M.; Rabideau, P. W.; Scott, L. T. *Science* **1994**, *265*, 1065. (c) Baumgarten, M.; Gherghel, J. L.; Wagner, M.; Weitz, A.; Rabinovitz, M.; Cheng, P.-C.; Scott, L. T. *J. Am. Chem. Soc.* **1995**, *117*, 6254. (d) Zabula, A. V.; Filatov, A. S.; Spisak, S. N.; Rogachev, A. Y.; Petrukhina, M. A. *Science* **2011**, *333*, 1008. (e) Spisak, S. N.; Zabula, A. V.; Filatov, A. S.; Rogachev, A. Y.; Petrukhina, M. A. *Angew. Chem., Int. Ed.* **2011**, *50*, 8090. (f) Zabula, A. V.; Spisak, S. N.; Filatov, A. S.; Petrukhina, M. A. *Angew. Chem., Int. Ed.* **2012**, *51*, 12194. (g) Filatov, A. S.; Zabula, A. V.; Spisak, S. N.; Rogachev, A. Y.; Petrukhina, M. A. *Angew. Chem., Int. Ed.* **2014**, *53*, 140.

(9) (a) Amaya, T.; Sakane, H.; Hirao, T. *Angew. Chem., Int. Ed.* **2007**, *46*, 8376. (b) Sakane, H.; Amaya, T.; Moriuchi, T.; Hirao, T. *Angew. Chem., Int. Ed.* **2009**, *48*, 1640. (c) Zanello, P.; Fedi, S.; de Biani, F. F.; Giorgi, G.; Amaya, T.; Sakane, H.; Hirao, T. *Dalton Trans.* **2009**, 9192. (d) Amaya, T.; Wang, W.-Z.; Sakane, H.; Moriuchi, T.; Hirao, T. *Angew. Chem., Int. Ed.* **2010**, *49*, 403. (e) Hirao, T.; Amaya, T.; Moriuchi, T.; Hifumi, M.; Takahashi, Y.; Nowik, I.; Herber, R. H. *J. Organomet. Chem.* **2011**, *696*, 3895.

(10) (a) Chin, R. M.; Jarosh, M. S.; Russell, J. D.; Lachicotte, R. J. *Organometallics* **2002**, *21*, 2027. (b) Chin, M.; Schelleneberg, J. *Eur. Polym. J.* **2007**, *43*, 2165.

(11) For an account: Nakamura, E. *J. Organomet. Chem.* **2004**, *689*, 4630.

(12) Marczak, R.; Wielopolski, M.; Gayathri, S. S.; Guldi, D. M.; Matsuo, Y.; Matsuo, K.; Tahara, K.; Nakamura, E. *J. Am. Chem. Soc.* **2008**, *130*, 16207.

(13) Sakurai, H.; Daiko, T.; Sakane, H.; Amaya, T.; Hirao, T. *J. Am. Chem. Soc.* **2005**, *127*, 11580.

(14) Alt, H. G.; Samuel, E. *Chem. Soc. Rev.* **1998**, *27*, 323.

(15) Schmid, M. A.; Alt, H. G.; Milius, W. *J. Organomet. Chem.* **1995**, *501*, 101.

(16) Schmid, M. A.; Alt, H. G.; Milius, W. *J. Organomet. Chem.* **1996**, *525*, 9.

(17) Crystal data for **2a**: monoclinic, space group $P2_1/c$ (#14), $a = 16.455(3)$ Å, $b = 8.545(2)$ Å, $c = 14.410(3)$ Å, $\beta = 106.740(3)^\circ$, $V = 1940.4(6)$ Å³, $Z = 4$; $R1 = 0.0505$; $wR2 = 0.1517$. The data have been deposited with the Cambridge Crystallographic Data Centre: CCDC-1004629.

(18) Crystal data for **2b**: monoclinic, space group $P2_1/c$ (#14), $a = 8.234(5)$ Å, $b = 16.024(9)$ Å, $c = 9.166(5)$ Å, $\beta = 95.38(2)^\circ$, $V =$

$1204(1)$ Å³, $Z = 2$; $R1 = 0.0348$; $wR2 = 0.1163$. The data have been deposited with the Cambridge Crystallographic Data Centre: CCDC-1004630.

(19) Haddon, R. C. *J. Am. Chem. Soc.* **1987**, *109*, 1676.

(20) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, Revision C.01; Gaussian, Inc.: Wallingford, CT, 2009.

(21) For reviews: (a) Kaminsky, W. *Catal. Today* **1994**, *20*, 257. (b) Mhring, P. C.; Coville, N. J. *Coord. Chem. Rev.* **2006**, *250*, 18.

(22) For accounts: (a) Negishi, E. *Bull. Chem. Soc. Jpn.* **2007**, *80*, 233. (b) Negishi, E.; Wang, G.; Rao, H.; Xu, Z. *J. Org. Chem.* **2010**, *75*, 3151.

(23) For a review: Chirik, P. J. *Organometallics* **2010**, *29*, 1500.